International Journal of Pharmaceutics, 58 (1990) 135–142
Elsevier

IJP 01971

Swelling and mechanical properties of poly(vinyl alcohol) hydrogels

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(Received 25 November 1987)
(Modified version received 3 July 1989)
(Accepted 7 August 1989)

Key words: Hydrogel; Poly(vinyl alcohol); Swelling; Viscoelastic behavior; Freeze-thaw cycle

Summary

Poly(vinyl alcohol) (PVA) aqueous solutions (of high water content) were repeatedly frozen and thawed to obtain PVA hydrogels. Both the degree of cross-linking and the viscoelastic behavior of the network structure in the PVA hydrogels varied directly as a function of the number of freeze-thaw cycles, as well as the thawing temperature.

Swelling kinetics of these PVA hydrogels in water were studied by weighing hydrogels swollen with water at various temperatures and time points. The rate of swelling of PVA hydrogels linearly increased with the square root of immersion time in water. A comparison of the amount of water in the swollen PVA matrix with the variation in the storage modulus of PVA hydrogels demonstrated a tendency for decrease in water absorption, as well as an increase in elasticity, with increasing cross-link density and network structure formation in these PVA hydrogels.

The rate coefficients of swelling, defined as the change in the absorbed amount of water in the hydrogel vs. the square root of immersion time, increased with increasing temperature of the swelling procedure.

Introduction

Cross-linked poly (vinyl alcohol) (PVA) hydrogels have been prepared by electron beam irradiation methods (Peppas and Merrile, 1977b) and by bulk mixing with cross linking agents such as sodium borate and boric acid. Watase (1983) and Geng and Ikada (1986) have proven the utility of preparing PVA hydrogels by repeatedly freezing and thawing PVA aqueous solutions. These hydrogels have been shown to be of high water content and elastic mechanical character.

A number of investigators (e.g. Peppas an Merrile, 1977a) are developing PVA hydrogels for biomedical applications, particularly transdermal drug delivery systems, because of inherent low toxicity, good biocompatibility and desirable physical properties such as rubbery or elastic nature and high degrees of swelling in water. Previously we have reported the relationship between PVA viscoelasticity and tack in order to use PVA

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as a vehicle for poultices (Urushizaki et al., 1986). In the previous work, a correlation between hydrogel tack and viscoelasticity (such as storage modulus and/or loss tangent) of PVA hydrogels was demonstrated using a multiregression analysis method.

Knowledge relating to the transport of water in PVA hydrogels is needed to improve the applications of these materials as artificial organs, implantable drug delivery systems and vehicles of poultices. In the present study, swelling and mechanical properties of PVA hydrogels prepared by repeatedly freezing and thawing PVA aqueous solution were evaluated to get some informations of water transport in the PVA hydrogels. The temperature dependency and effect of additives on the swelling behavior were also investigated.

Materials and Methods

Materials

All experiments utilized commercial grade PVA (Denka Poval K-20, Asahidenka Co., Ltd.) having a number-average molecular weight of about 80000 and a saponification value of greater than 98.0%.

Preparation of PVA hydrogels

PVA hydrogels were prepared by repeatedly freezing and thawing 15% aqueous solution of PVA. The solution was frozen for 16 h at −25 °C followed by thawing at various temperatures followed by repeated cycles. The freeze-thaw cycle was also varied to change the properties of the resulting PVA hydrogels.

Degree of cross-linking of PVA

Differences in the weight changes of the dried PVA gels from the rinsed and unrinsed conditions per volume of the same hydrogel can be assumed as an index of the degree of cross-linking. The index was calculated as follows:

$$\text{Degree of cross-linking (\%)} = \frac{W_i - W_f}{W_i} \times 100$$

where W_i and W_f are the weights of the dried PVA hydrogel before and after rinsing and extraction. Slices of approximately 10 g of PVA hydrogels were weighed and then dried under vacuum at room temperature until the dried mass showed constant weight. Nearly identical weights of another slice of the same PVA hydrogel were weighed and then immersed into 3 liters of distilled water. Distilled water (3 l) was renewed every day for 3 days to rinse away unreacted materials. Subsequently, the block of gel was removed from the rinse water, dried at room temperature under vacuum until all water was removed and weighed.

Scanning electron microscopy of PVA hydrogel

The network structures of PVA hydrogels were observed and compared by using a scanning electron microscope (SEM). Small, thin blocks of PVA hydrogel were cut and immersed in small amounts (10 ml) of distilled water. Ethanol was then added to this water in which the gel slice was immersed and the content of ethanol was increased gradually, similar to the method of sample preparation for SEM (Higashi and Tooyama, 1979). During this treatment, the PVA hydrogel became physically more rigid and apparently more opaque compared with the original PVA hydrogel in water. The block of PVA hydrogel was then attached to the vacuum system to dry and was subsequently sputtered with gold before observation under a Hitachi scanning electron microscope

Measurement of swelling of PVA hydrogel

Rates of swelling of PVA hydrogels in distilled water were studied by weighing the increase in water content in gel samples molded in plastic cups and immersed in 50 ml of distilled water. Gel disks (5.1 cm diameter, 1.3 cm thickness) were weighed after gentle surface wiping using absorbent paper. Swelling was monitored at 5, 21, 35 and 50 °C in either pure distilled water, 0.9% NaCl solution or various concentrations of PVA aqueous solution. The degree of swelling was calculated using the following equation:

$$\text{Degree of swelling (\%)} = \frac{W_s - W_d}{W_d} \times 100$$

where W_d is final dry weight of the extracted PVA hydrogel and W_d is swollen weight of the same PVA hydrogel at immersion time (t) in distilled water.

Measurement of dynamic viscoelasticity of PVA hydrogel

Dynamic viscoelasticity parameters including storage modulus, loss modulus and loss tangent were measured using a Rheolograph-gel (Toyo Seiki Co., Ltd.). Hydrated PVA hydrogel rods (20 mm diameter, 30 mm length) weighing 10 g were subjected to 100 μm mechanical vibrating amplitude at a frequency of 2 Hz at various temperatures.

Results and Discussion

PVA hydrogel preparation and network structure

PVA hydrogels were made by repeated cycles of freezing and thawing of 15% PVA aqueous solutions. We have noted previously (Urushizaki et al.,l 1986) that PVA hydrogels became harder and more rigid when the number of cycles of freezing and thawing was increased. PVA components which are not incorporated into the network structure of the resulting hydrogel are thought to be washed out during the rinse procedure.

Scanning electron micrographs of the PVA hydrogels after varying numbers of freeze-thaw cycles are shown in Fig. 1. Aqueous PVA solutions used as controls, which were not treated with repeated freezing and thawing, had no network structure and resembled a tacky resin (Fig. 1A). Hydrogel network structures, however, could be seen under SEM when aqueous solutions of PVA were cycled through repeated freezing and thawing (Fig. 1B). More cycles of freezing and thawing caused the network structure to become increasingly dense and entangled (Fig. 1C).

Figure 2 shows the effect of the number of freeze-thaw cycles on the degree of cross-linking and elasticity (mechanical storage modulus) of PVA hydrogel. The degree of cross-linking tended to decrease with increasing number of freeze-thaw cycles. About 10.6% of the total PVA in the original solution was not incorporated after one cycle of freezing and thawing. It was assumed that the remaining 89.4% of the PVA might contribute to the hydrogel network structure. After 4 freeze-thaw cycles, the amount of not incorporated PVA decreased to 7.0%. The contribution of PVA to the hydrogel network structure increased with increasing number of cycles of freezing and thawing.

Elasticities of PVA hydrogels determined by measuring the mechanical storage modulus, were affected by the number of freeze-thaw cycles (Fig.

Fig. 1. Scanning electron micrographs of PVA hydrogel networks. (A) Non-gelation; (B) 1-cycle; (C) 4-cycle.

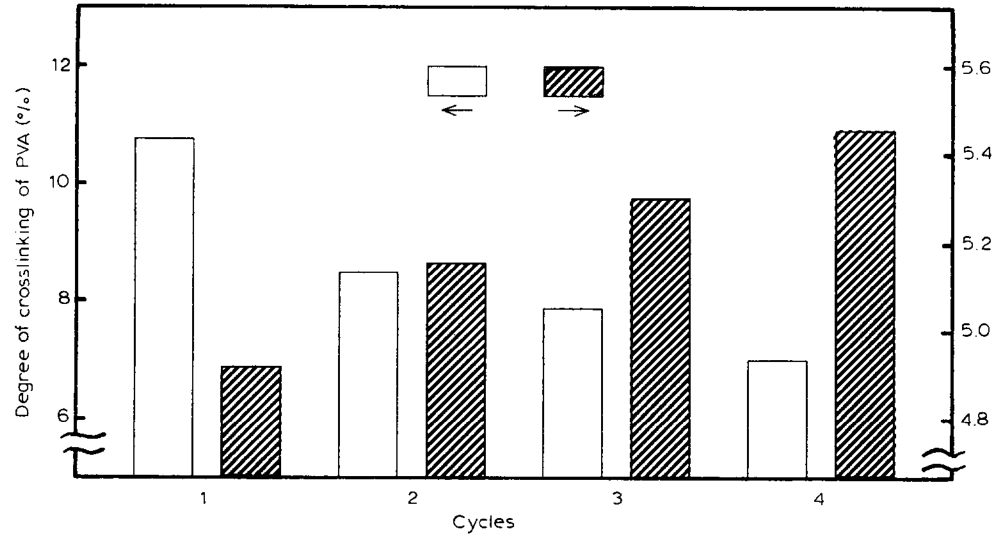

Fig. 2. Effect of freeze-thaw cycle on the degree of cross-linking and mechanical storage modulus of PVA hydrogels.

2). PVA hydrogels were harder with increased rigidity when the number of freeze-thaw cycles was increased. It is rationalized that each cycle induces an increasing proportion of unincorporated, soluble PVA to contribute to the network structure of the PVA hdyrogel, causing an increase in the entanglement and density of the network structure.

Swelling of PVA hydrogels

SEM micrographs and physical property changes demonstrate that the PVA network structure changes by freezing and thawing conditions. Swelling characteristics, particularly the rate of aqueous swelling or water uptake, were anticipated to change with variations in the freeze-thaw procedure.

Figure 3 shows degrees of swelling for the PVA hydrogels vs. the square root of immersion time Excellent linear correlations were observed be-

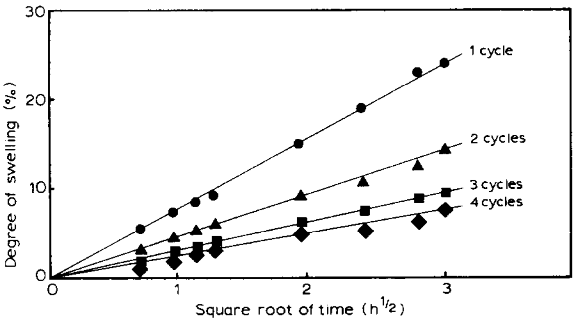

Fig. 3. Effect of freeze-thaw cycle on the time course of swelling of PVA hydrogels.

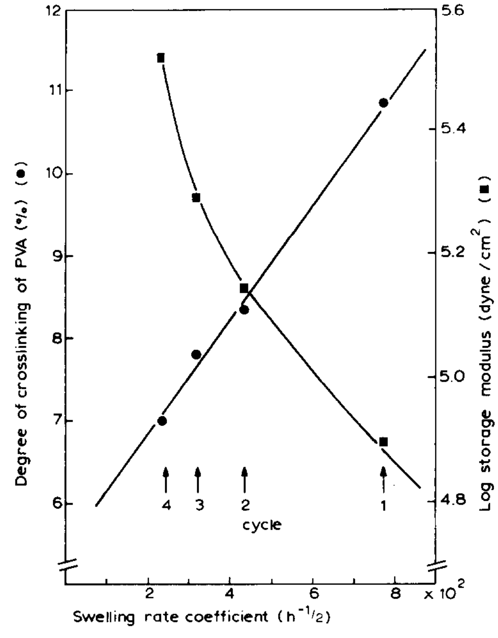

Fig. 4. Plot of degree of cross-linking and mechanical storage modulus vs. swelling rate coefficients of PVA hydrogels.

tween the degree of swelling and the square root of immersion time for all gelation cycles. Hsieh and Chien (1985) have previously published a similar pattern of swelling phenomena for early stages of glycerol absorption into silicone elastomers. Degrees of swelling consistently decrease with increasing numbers of freeze-thaw cycles. In every swelling measurement, the amounts of not incorporated PVA washed out (degrees of cross-linking of PVA) were relatively small and were neglected in the swelling calculations. Linear slopes of all PVA hydrogel-swelling behaviors in Fig. 3 were assumed to represent relative swelling rate coefficients. The swelling rate coefficient was calculated by dividing the slope in Fig. 3 by 100. Relationships between those calculated swelling rate coefficients and the degree of cross-linking of PVA in hydrogels are shown in Fig. 4. Correlations between the swelling rate coefficients and viscoelastic moduli of PVA hydrogels are also shown in the figure. Swelling rate coefficients of PVA hydrogels linearly increased by increasing the degree of cross-linking of PVA in hydrogel matrices and they decreased with the storage modulus.

Peppas and Merrile (1977b), Westman and Linderstrom (1981) and John et al. (1976) have reported relationships between swelling behaviors of various hydrogels and their viscoelastic properties. Peppas and John and co-workers utilized primarily tensile strength while Westman and Linderstrom investigated creep compliance as viscoelastic parameters. There are almost no papers concerned with the relation between swelling characteristics of hydrogels and their dynamic viscoelastic behaviors as represented by mechanical storage modulus, loss modulus and loss tangent. Peppas and Merrile (1977b) have presented an equation derived from Flory's original swelling theory (Flory et al., 1949). This equation was used for evaluating the relationship between tensile stress and hydrogel swelling ratios under thermodynamic equilibrium conditions in swelling solvents. Tensile stress was shown to be linearly related to the reciprocal cubic root of the swelling ratio. This procedure also analyzed thermodynamic kinetic processes and showed that the logarithmic storage modulus was linearly related to the reciprocal cubic root of the swelling rate coefficient.

Temperature dependency on swelling characteristics of PVA hydrogels

Swelling characteristics of the same PVA hydrogels were investigated under various swelling conditions. Figure 5 demonstrates that water uptake upon swelling (degree fo swelling) increases with increasing temperature. In addition, swelling rate coefficients were also derived from the slopes of plots of swelling degrees vs. the square root of immersion time at various temperatures (Fig. 5A), and plotted against reciprocal absolute temperature (similar to an Arrhenius-type plot) (Fig. 5B). Swelling rate coefficients at 5, 21 and 35 ° C showed a linear relationship to reciprocal absolute temperature but the coefficient at 50 ° C showed some deviation from this line.

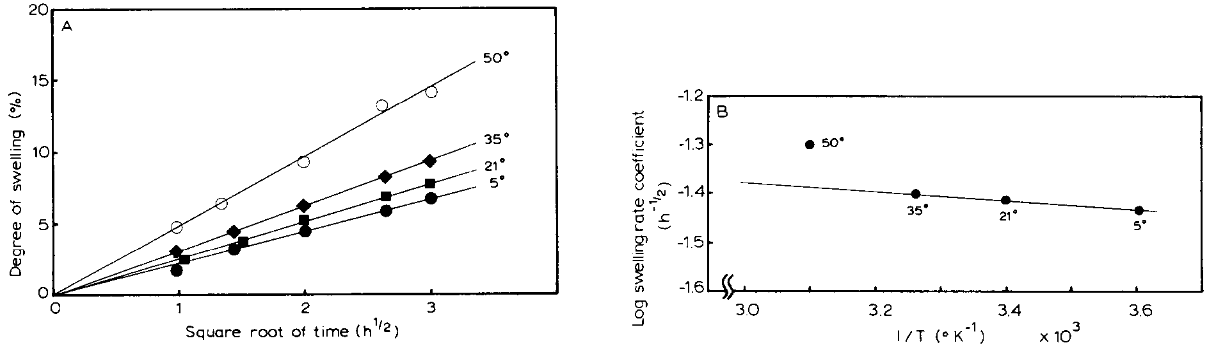

Fig. 5. Temperature dependency of swelling for PVA hydrogels. (A) Time course of degree of swelling; (B) Arrhenius-type plots of swelling kinetics.

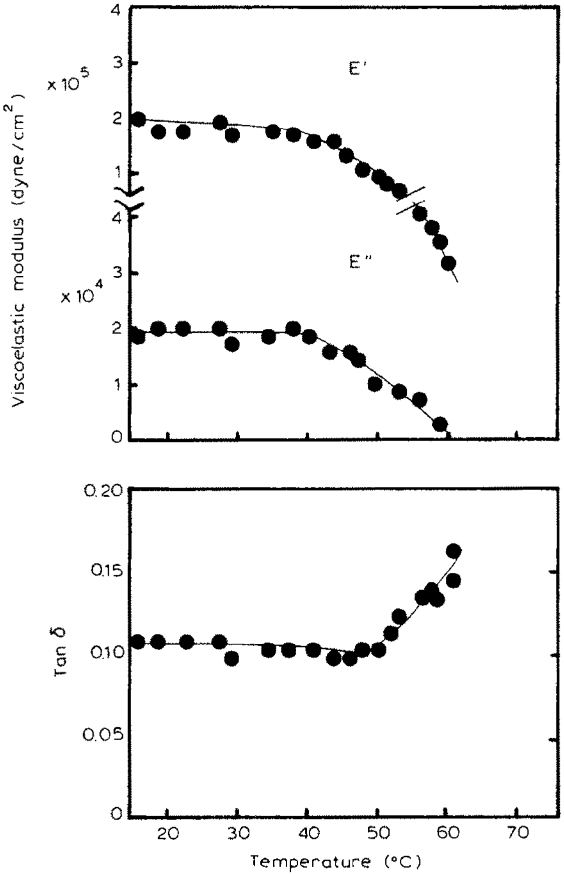

Fig. 6. Temperature dependency of viscoelasticities for PVA hydrogels. E′ = storage modulus, E″ = loss modulus, tan δ = loss tangent.

Furthermore, viscoelasticities of hydrated PVA hydrogels based on storage modulus, loss modulus and loss tangent were measured at various temperatures. Figure 6 shows a plot of these mechanical viscoelastic parameters as a function of temperature. Viscoelasticities changed little from 15 °C to about 50 °C but began to change above 50 °C because of an observed irreversible physical change from gel to sol. The deviation of swelling rate coefficients at 50 °C (Fig. 5) might be attributed to this change. Increasing swelling ability observed from 5 to 35 °C (Fig. 5) was possibly associated with the anticipated thermodynamic activity change of the solvent between those temperatures but apparently did not affect a physical change in the PVA hydrogel.

Hydrogel swelling characteristics using soluble additives in immersing solutions

Fig. 7 shows some examples of swelling characteristics when some additives are used in immersing solutions. Specifically, 0.9% NaCl and various concentrations of solubilized PVA were used for electrolyte and nonelectrolyte immersion solutions, respectively. Figure 7 represents data collected from hydrogel samples created by 3 freeze-thaw cycles. Degree of swelling vs. square root of immersion time demonstrated good linearity. When electrolyte (NaCl) was present in the immersing solution, the swelling ability enhanced over swelling in pure solvent. In the nonelectrolyte case (PVA), the slopes of these plots, indicating swelling abilities, suppressed with increasing concentration of PVA additive.

Finally, shrinking of the PVA hydrogel was observed at 12% PVA concentration in the immersing solution. The concentration (12%) corresponded to nearly the same concentration of solubilized PVA present after PVA hydrogel formation during various freeze-thaw conditions. Little difference was noted between the concentration of PVA, washed out from the hydrogel during gelation and the PVA concentration in the immersion solution, needed to induce hydrogel shrinking.

Swelling characteristic and spin-lattice relaxation

Nagura et al. (1985) have reported the relationships between spin-latice or thermographical

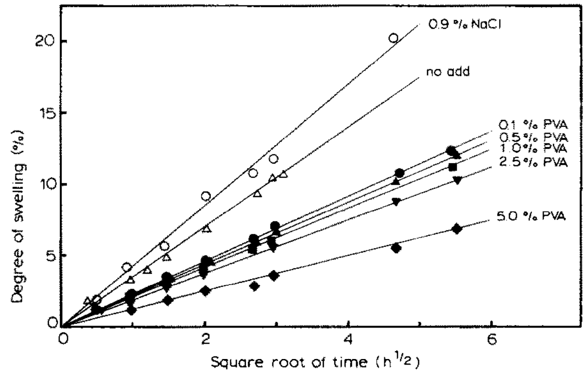

Fig. 7. Effect of additives in immersing solution on swelling kinetics.

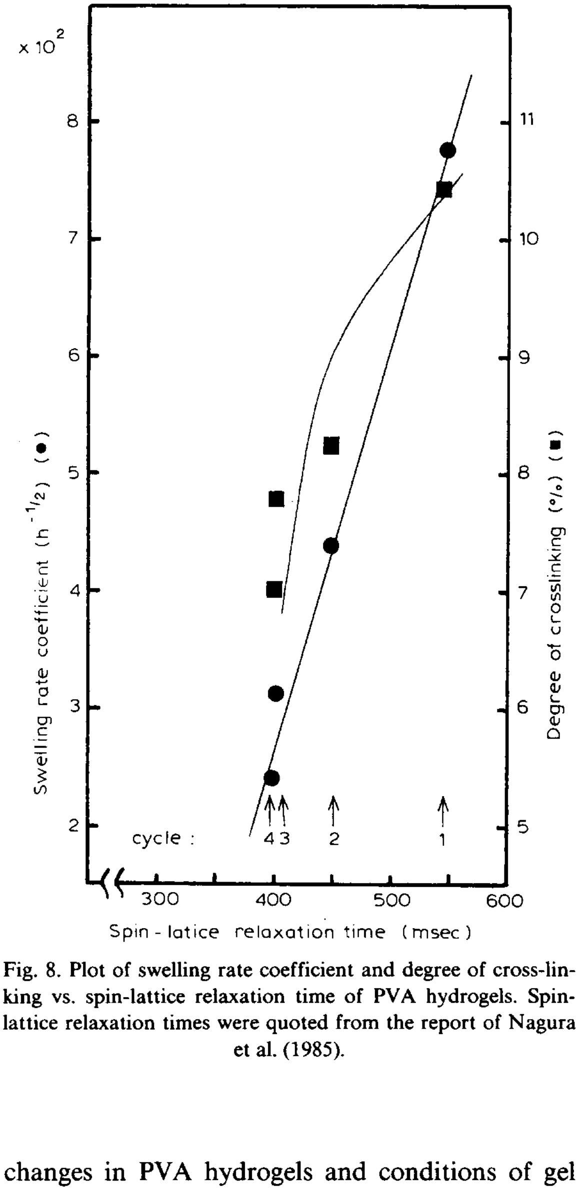

Fig. 8. Plot of swelling rate coefficient and degree of cross-linking vs. spin-lattice relaxation time of PVA hydrogels. Spin-lattice relaxation times were quoted from the report of Nagura et al. (1985).

changes in PVA hydrogels and conditions of gel formation such as freeze-thaw cycles. Their opinion regarding hardening phenomena in the viscoelasticity of PVA hydrogels with different gelation conditions was that the freeze-thaw procedure increasingly restricted the movement and content of water in the PVA network. Comparison of our swelling experiments and the results of Nagura et al. of spin-lattice relaxation are consistent in demonstrating the various interactions between PVA networks and water. These interactions may be explained in terms of degree of water–matrix association, i.e., bound water, free water and unfrozen water (Katayama 1986).

Figure 8 shows the linear relation between Nagura et al.'s data on spin-lattice relaxation and our data on swelling coefficients of PVA hydrogels. As previously mentioned above, amounts of PVA washed out from hydrogel networks (degree of cross-linking of PVA hydrogels) decreased with increasing numbers of freeze-thaw cycles. Changes in spin-lattice relaxation time under varying freeze-thaw conditions might be affected as well by degrees of cross-linking of PVA hydrogels (Fig. 8).

Conclusions

From this discussion, we conclude that there are close relations between unincorporated PVA, extracted from PVA hydrogel networks, density of the resulting network structure, hydrogel viscoelasticity, swelling characteristics and spin-lattice relaxation times. Amounts of PVA not incorporated in PVA networks (degree of cross-linking of PVA) during freeze-thaw cycling might result from the increased matrix swelling after a certain critical percent of PVA chains become incorporated in developing matrices. This swelling and an excess bulk of water in the network may prevent further PVA from incorporating in to the freeze-thaw-derived network. This critical degree of matrix conversion results in networks of specific density and physical entanglement that maintain the observed degree of water association, viscoelasticity and swelling character.

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